# *PYROX Process Development*


**Mark A. Williamson**

**Chemical Technology Division**

**Argonne National Laboratory**


**AFCI Review Meeting**

**Albuquerque, NM**

**January 22-24, 2003**

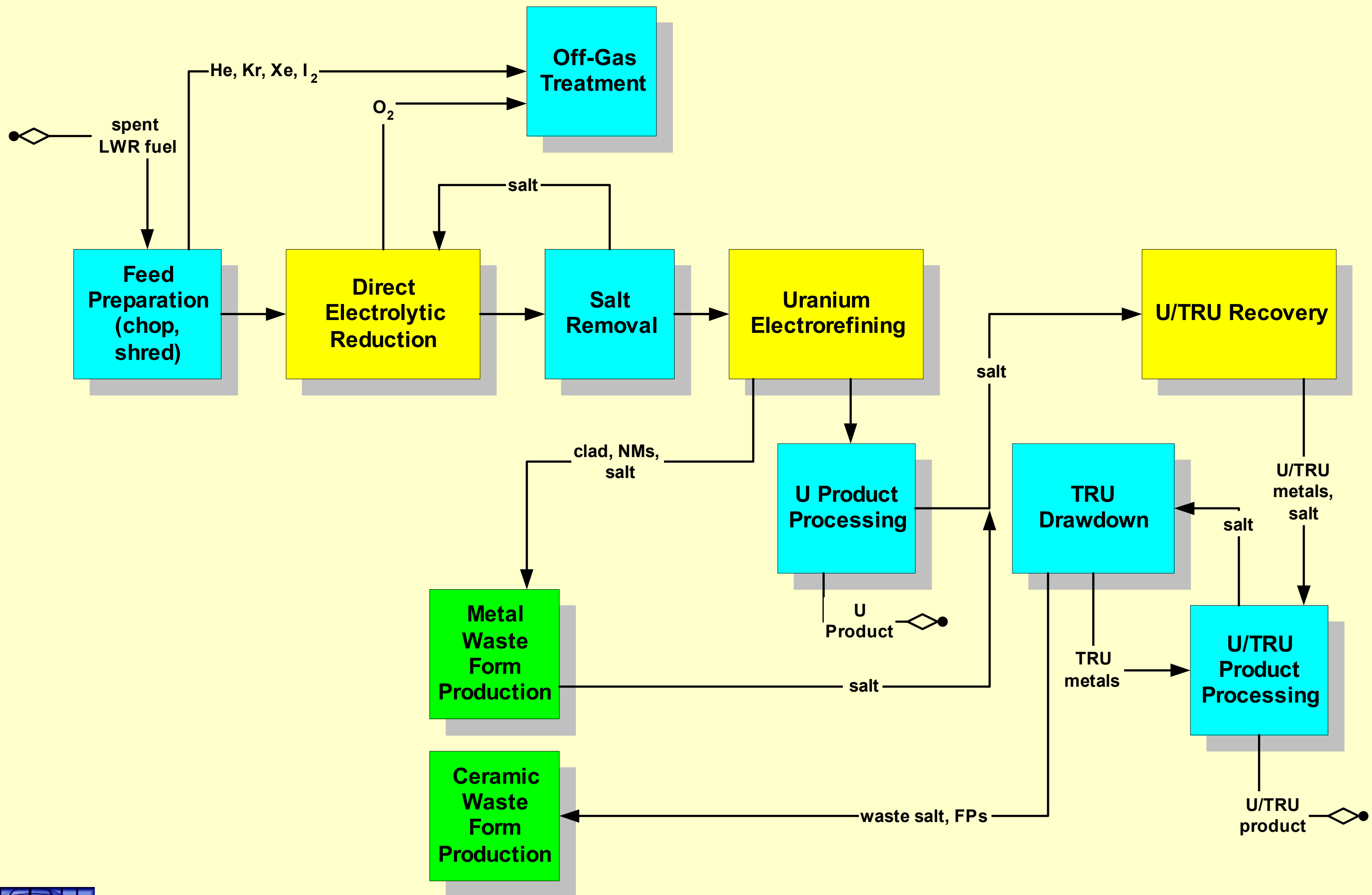
# *Goal*

**Develop a commercially viable pyrochemical process for treating spent light water reactor fuel providing actinides for recycle to advanced reactor systems**

**Development efforts focused on three unit operations**

- **Reduction of oxide fuel**
- **High-throughput uranium electrorefining**
- **Transuranic element recovery**

# *PYROX Process Flowsheet*

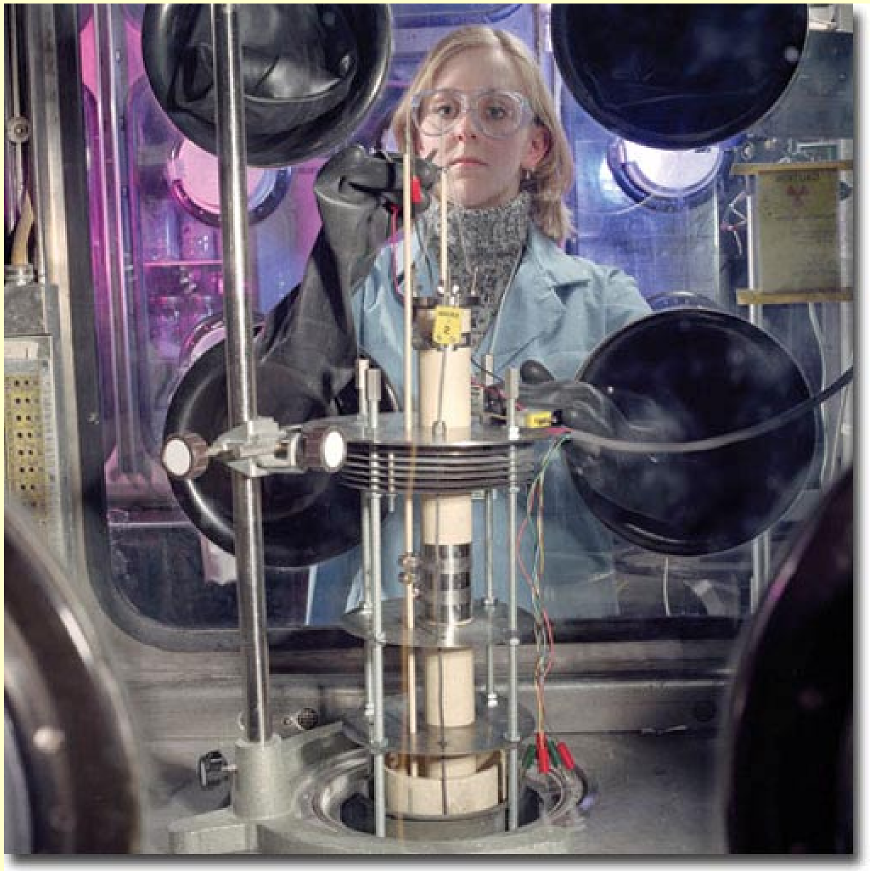



*Argonne National Laboratory*
*Chemical Technology Division*

# *Oxide Reduction Process*

**Electrochemical process selected for reducing spent fuel oxides to metals**

- – **High product quality**
- – **High throughput**
- – **Simple engineering**



- **Cathode process**

  $$MO_X\,(s) + 2xe^- = M\,(s) + x\,O^{2-}$$

- **Anode process**

  $$2\,O^{2-} = O_2\,(g) + 4\,e^-$$

# *Electrolytic Process Development: Progress*

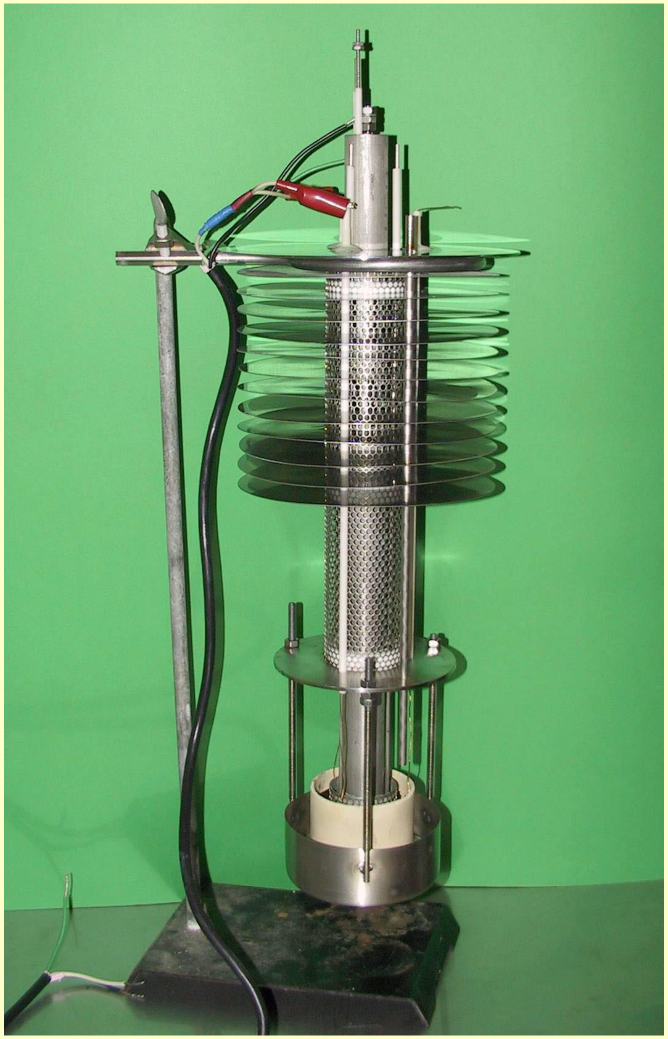
- **Process viability proven with $UO_2$ at laboratory scale (~20-350 g)**
  - **Routinely achieve complete reduction of $UO_2$**
  - **Two cell concepts being investigated; both perform well**
  - **No deleterious effects from alkali and alkaline earth elements in feed**
  - **Other fission product elements being investigated, no problems yet seen**

- **Successfully demonstrated reduction of mixed oxide fuel ($UO_2$ - 5wt% $PuO_2$)**
  - **Complete conversion of actinide oxides to base metals, including americium oxide**

- **Reduction rates are very good**
  - **Cells designed for collecting fundamental data, not optimized for rate**

- **Methods devised for analysis of reduction product**
  - **Combustion analysis**
  - **Bromination in ethyl acetate / ICP-AE analysis**

# Reduction Cell and Product



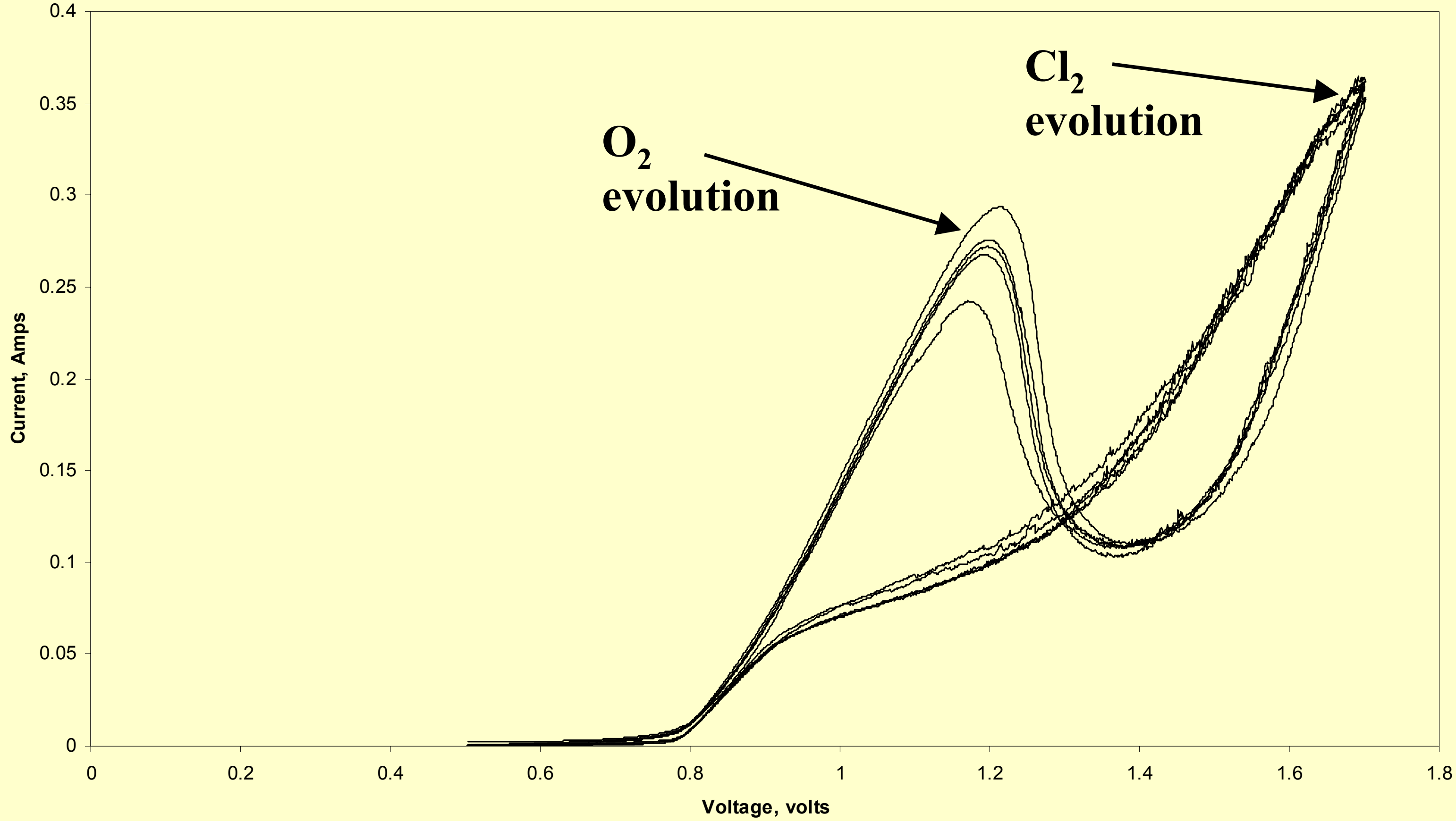
# *Anode Development*

- **Material selection**
  - **Thermodynamic assessments**
  - **Industrial and prior Laboratory experience**
    - **Pt, Au, doped $SnO_2$, $Li_2SnO_3$, $LiFeO_2$, $CoFe_2O_3$, $BaCrO_4$, $RuO_2$, and $SrRuO_3$**

- **Materials fabrication**
  - **Fabrication issues sidelined testing monolithic $Li_2SnO_3$, $RuO_2$ and $SrRuO_3$**
  - **Composite ceramics of $SrRuO_3$ and $RuO_2$ fabricated**
  - **Optimization of fabrication process for composite material underway**

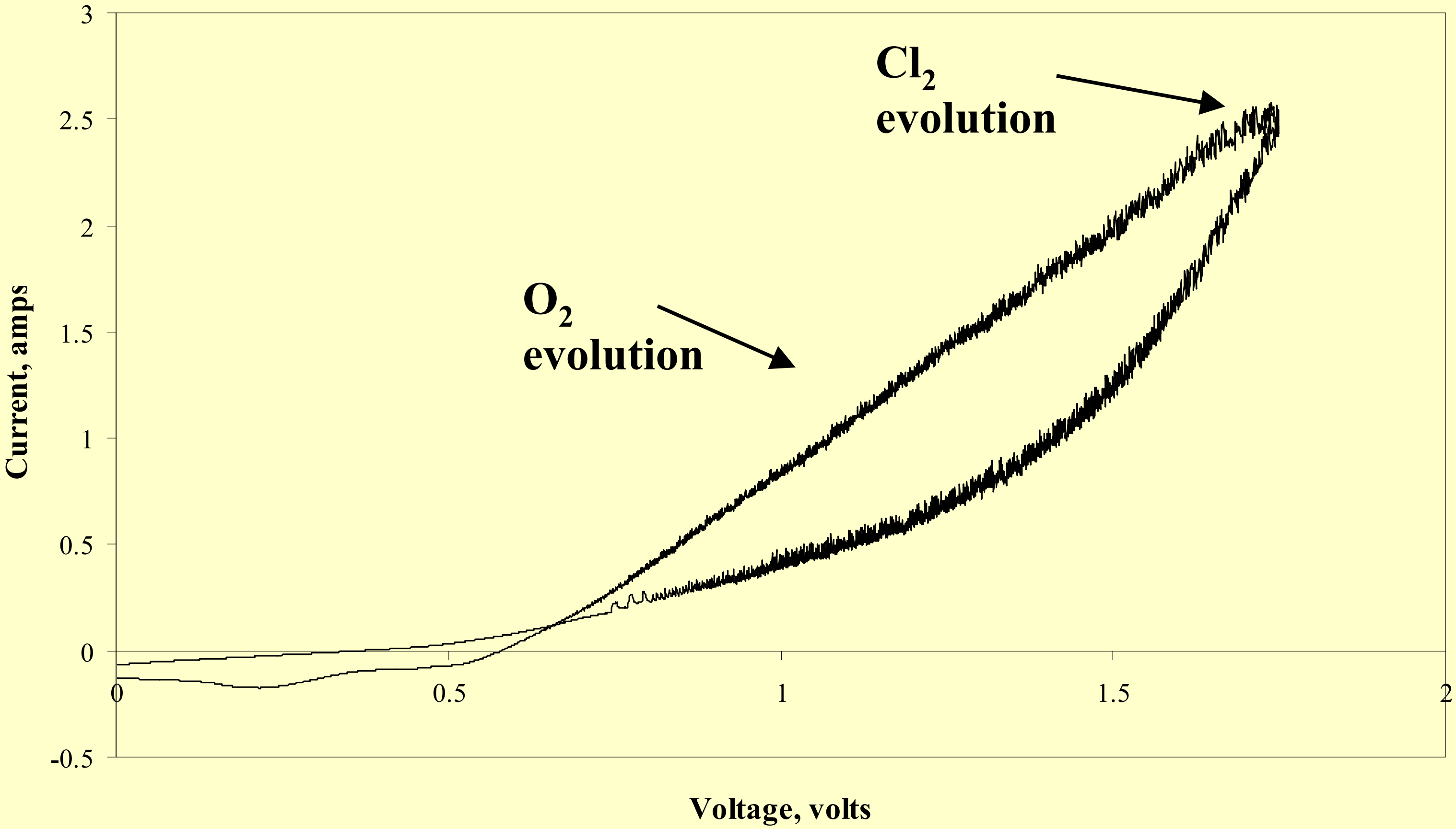
- **Anode material evaluation**
  - **Chemical exposure tests in LiCl-$Li_2O$ at 650°C**
    - **$BaCrO_4$ eliminated**
  - **Electrical conductivity at temperature (pure materials)**
  - **Cyclic voltammetry**
  - **Current behavior at constant voltage**

# *Anode Material Evaluation*



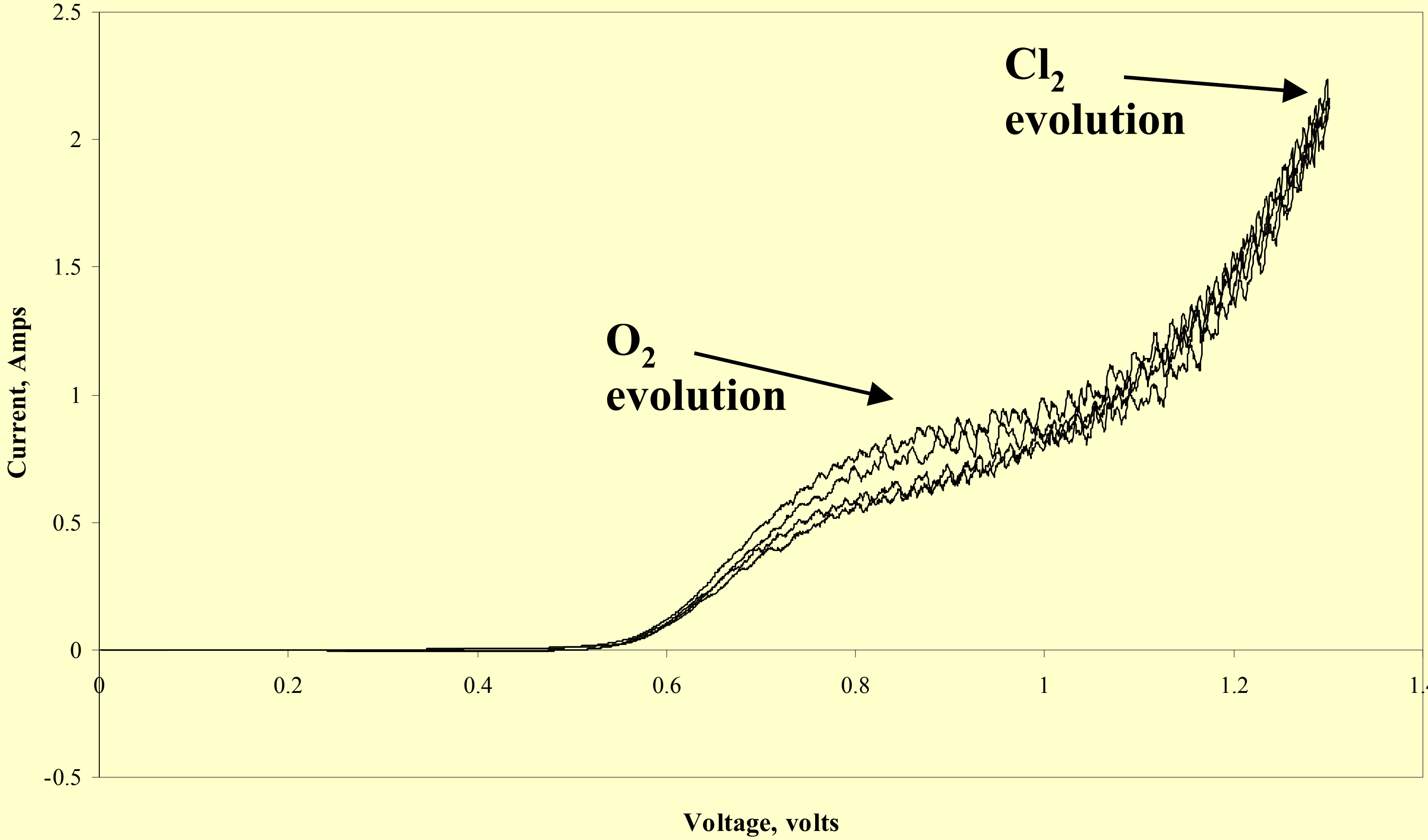

**Cyclic voltammogram for Au wire, LiCl – 1 wt% $Li_2O$ at 650°C, 5 mV/s scan rate, Ni/NiO reference electrode**

# *Anode Material Evaluation (cont.)*



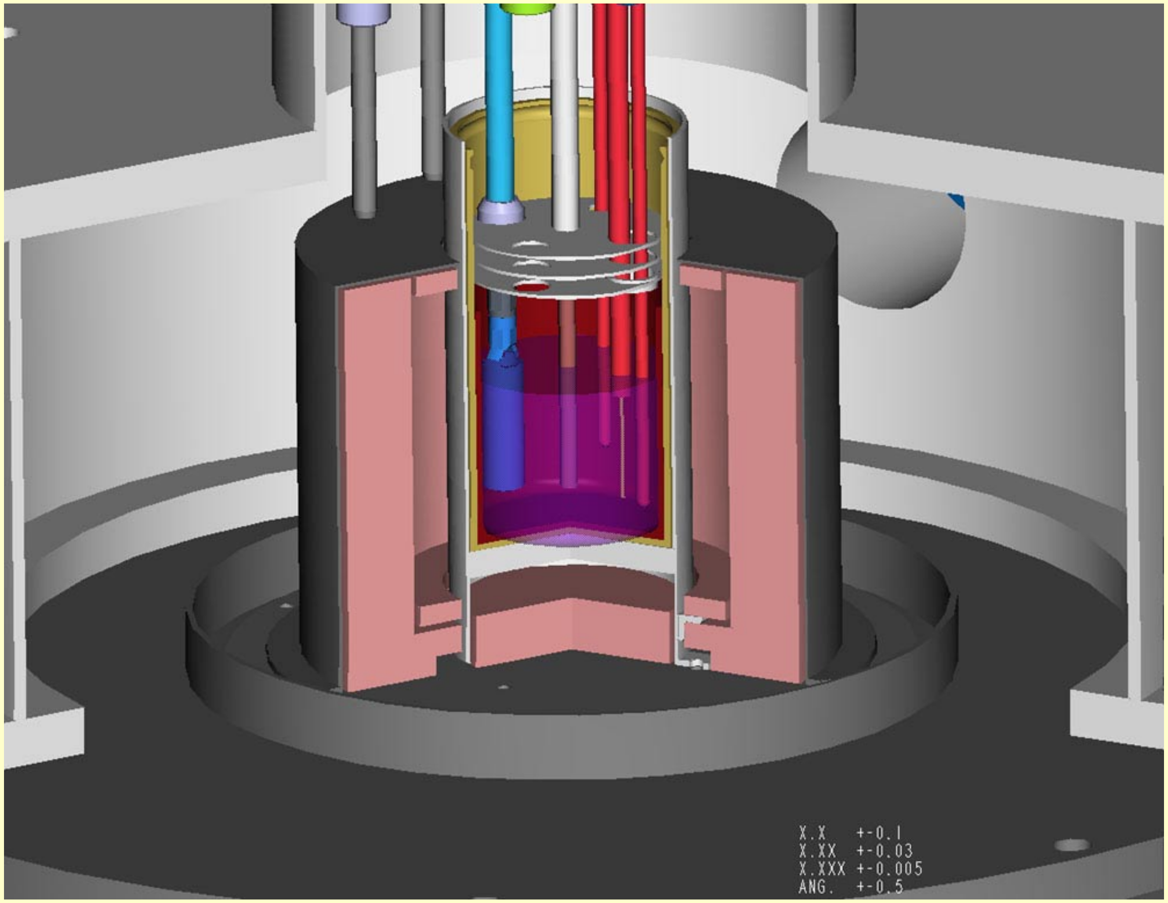

**Cyclic voltammogram for $SrRuO_3$ composite, LiCl – 1 wt% $Li_2O$ at 650°C, 5 mV/s scan rate, Ni/NiO reference electrode**

# *Anode Material Evaluation (cont.)*




**Cyclic voltammogram for Au disk, LiCl – 1 wt% $Li_2O$ at 650°C, 5 mV/s scan rate, Ni/NiO reference electrode**

# *Irradiated Fuel Reduction Demonstration*




**Electrolytic cell being fabricated for demonstration of oxide reduction process with irradiated fuel at ANL-ID**

# *Process Modeling and Cell Design*

**Develop an electrochemical model that simulates laboratory-scale cells and use the model as a tool to design scale-cells**

- **Model**
  - **Combines thermodynamic, kinetic, and transport phenomena through a set of nonlinear coupled differential equations that can be solved numerically**
  - **Determines the current, potential, concentration, temperature, and flow distributions inside an electrochemical cell**
  - **Demonstrated as a valuable tool for electrochemical systems to accurately account for changes in scale**

- **Input to electrochemical model**
  - **Physical parameters, thermodynamic information and conductivities obtained from literature**
  - **Kinetic rate constants determined from cyclic voltammetry of anode materials and $UO_2$ electrodes**
  - **Gas evolution characteristics at anode along with oxide and lithium transport parameters will be inferred from simulations of laboratory-scale studies**

# *Process Modeling and Cell Design: Progress*

- **Developed electrochemical model for $UO_2$ electrode in laboratory-scale cell geometries**
- **Conducting initial simulation studies to insure understanding of $UO_2$ reduction process mechanism and to establish unknown parameter values**
- **Initiated fluid dynamics calculations for mass transport of oxide ions from $UO_2$ electrode to anode**

# *Future Directions*

- Scale-cell design and testing with $UO_2$ and mock fuel
  - Target size: 100 kg HM with oxygen gas handling capability
  - Refine process model
  - Select cell concept for further development
- Anode materials development and testing
  - Optimize fabrication parameters (Particle size, T, t)
  - Produce monolithic ceramic and composite anodes
  - In-cell evaluation of most promising materials
- Laboratory-scale tests (50-500 g HM)
  - Evaluate fission product behavior
    - Te, I, Se
    - Rare earth, Y
  - Materials test-bed
    - Identify and evaluate materials of construction

# *Acknowledgements*

**PYROX process development is accomplished with staff from the following Divisions at Argonne:**

- **Chemical Technology**
  - **Nuclear Technology Department**
  - **Engineering Research Section of Battery Department**

- **Engineering Technology**
  - **Fuel Cycle Technology Section**